
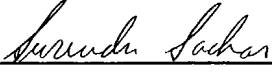


FORM PTO-1390 (Modified) (REV 11-2000)		U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER 220983US0PCT	
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371				U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 10/089109)	
INTERNATIONAL APPLICATION NO. PCT/JP00/06959		INTERNATIONAL FILING DATE 05 OCTOBER 2000		PRIORITY DATE CLAIMED 08 OCTOBER 1999 (EARLIEST)	
TITLE OF INVENTION LITHIUM-COBALT COMPOSITE OXIDE, PROCESS FOR ITS PRODUCTION, POSITIVE ELECTRODE FOR LITHIUM SECONDARY CELL EMPLOYING IT, AND LITHIUM SECONDARY CELL					
APPLICANT(S) FOR DO/EO/US Manabu SUHARA, et al.					
Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:					
<ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below. 4. <input checked="" type="checkbox"/> The US has been elected by the expiration of 19 months from the priority date (Article 31). 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371 (c) (2)) <ol style="list-style-type: none"> a. <input type="checkbox"/> is attached hereto (required only if not communicated by the International Bureau). b. <input checked="" type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input checked="" type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). <ol style="list-style-type: none"> a. <input checked="" type="checkbox"/> is attached hereto. b. <input type="checkbox"/> has been previously submitted under 35 U.S.C. 154(d)(4). 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are attached hereto (required only if not communicated by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input checked="" type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)). 10. <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)). 11. <input checked="" type="checkbox"/> A copy of the International Preliminary Examination Report (PCT/IPEA/409). 12. <input checked="" type="checkbox"/> A copy of the International Search Report (PCT/ISA/210). 					
Items 13 to 20 below concern document(s) or information included: <ol style="list-style-type: none"> 13. <input checked="" type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 14. <input checked="" type="checkbox"/> An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 15. <input checked="" type="checkbox"/> A FIRST preliminary amendment. 16. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 17. <input type="checkbox"/> A substitute specification. 18. <input type="checkbox"/> A change of power of attorney and/or address letter. 19. <input type="checkbox"/> A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825. 20. <input type="checkbox"/> A second copy of the published international application under 35 U.S.C. 154(d)(4). 21. <input type="checkbox"/> A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4). 22. <input type="checkbox"/> Certificate of Mailing by Express Mail 23. <input checked="" type="checkbox"/> Other items or information: Notice of Priority / PCT/IB/304 / PCT/IB/308 PTO-1449 					

U.S. APPLICATION NO. (IF KNOWN, SEE 37 CFR 1.101) 10/089109		INTERNATIONAL APPLICATION NO. PCT/JP00/06959		ATTORNEY'S DOCKET NUMBER 220983US0PCT	
24. The following fees are submitted: BASIC NATIONAL FEE (37 CFR 1.492 (a) (1) - (5)) : <input type="checkbox"/> Neither international preliminary examination fee (37 CFR 1.482) nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO and International Search Report not prepared by the EPO or JPO \$1040.00 <input checked="" type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but International Search Report prepared by the EPO or JPO \$890.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) not paid to USPTO but international search fee (37 CFR 1.445(a)(2)) paid to USPTO \$740.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO but all claims did not satisfy provisions of PCT Article 33(1)-(4) \$710.00 <input type="checkbox"/> International preliminary examination fee (37 CFR 1.482) paid to USPTO and all claims satisfied provisions of PCT Article 33(1)-(4) \$100.00 ENTER APPROPRIATE BASIC FEE AMOUNT =				CALCULATIONS PTO USE ONLY	
Surcharge of \$130.00 for furnishing the oath or declaration later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (e)).				\$0.00	
CLAIMS	NUMBER FILED	NUMBER EXTRA	RATE		
Total claims	11 - 20 =	0	x \$18.00	\$0.00	
Independent claims	1 - 3 =	0	x \$84.00	\$0.00	
Multiple Dependent Claims (check if applicable).				<input type="checkbox"/>	\$0.00
TOTAL OF ABOVE CALCULATIONS				=	\$890.00
<input type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27). The fees indicated above are reduced by 1/2.				\$0.00	
SUBTOTAL				=	\$890.00
Processing fee of \$130.00 for furnishing the English translation later than <input type="checkbox"/> 20 <input type="checkbox"/> 30 months from the earliest claimed priority date (37 CFR 1.492 (f)).				\$0.00	
TOTAL NATIONAL FEE				=	\$890.00
Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31) (check if applicable).				<input checked="" type="checkbox"/>	\$40.00
TOTAL FEES ENCLOSED				=	\$930.00
				Amount to be refunded	\$
				charged	\$
a. <input checked="" type="checkbox"/> A check in the amount of \$930.00 to cover the above fees is enclosed. b. <input type="checkbox"/> Please charge my Deposit Account No. _____ in the amount of _____ to cover the above fees. A duplicate copy of this sheet is enclosed. c. <input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment to Deposit Account No. 15-0030 A duplicate copy of this sheet is enclosed. d. <input type="checkbox"/> Fees are to be charged to a credit card. WARNING: Information on this form may become public. Credit card information should not be included on this form. Provide credit card information and authorization on PTO-2038.					
NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or (b)) must be filed and granted to restore the application to pending status.					
SEND ALL CORRESPONDENCE TO:					
 22850 Surinder Sachar Registration No. 34,423 (703) 413-3000			 SIGNATURE Norman F. Oblon NAME 24,618 REGISTRATION NUMBER March 26 2002 DATE		

JC13 Rec'd PCT/PTO 26 MAR 2002

220983US-0PCT

IN THE UNITED STATES PATENT & TRADEMARK OFFICE

IN RE APPLICATION OF :
 MANABU SUHARA ET AL : ATTN: APPLICATION DIVISION
 SERIAL NO: NEW U.S. PCT APPLN :
 (Based on PCT/JP00/06959)
 FILED: HEREWITH :
 FOR: LITHIUM-COBALT COMPOSITE
 OXIDE, PROCESS FOR ITS
 PRODUCTION,
 POSITIVE ELECTRODE FOR
 LITHIUM SECONDARY CELL
 EMPLOYING IT, AND
 LITHIUM SECONDARY CELL

PRELIMINARY AMENDMENT

ASSISTANT COMMISSIONER FOR PATENTS
 WASHINGTON, D.C. 20231

SIR:

Prior to examination on the merits, please amend the above-identified application as follows.

IN THE CLAIMS

Please amend the claims as shown in the marked-up copy following this amendment to read as follows:

4. (Amended) The hexagonal lithium-cobalt composite oxide for a lithium secondary cell according to Claim 1, wherein the packing press density of the hexagonal lithium-cobalt composite oxide is from 2.90 to 3.35 g/cm³.

5. (Amended) A process for producing the hexagonal lithium-cobalt composite oxide for a lithium secondary cell as defined in Claim 1, which comprises dry blending a cobalt oxyhydroxide powder having an average particle size of from 1 to 20 μm and a specific surface area of from 2 to 200 m^2/g , a lithium carbonate powder having an average particle size of from 1 to 50 μm and a specific surface area of from 0.1 to 10 m^2/g , and a powder of an oxide of metal element M having an average particle size of at most 10 μm and a specific surface area of from 1 to 100 m^2/g , and firing the mixture at a temperature of from 850 to 1,000°C in an oxygen-containing atmosphere.

7. (Amended) A positive electrode for a lithium secondary cell, which contains the hexagonal lithium-cobalt composite oxide for a lithium secondary cell as defined in Claim 1, as an active material.

9. (Amended) The positive electrode for a lithium secondary cell according to Claim 7, wherein the current collector is aluminum or stainless steel.

10. (Amended) A lithium secondary cell employing a positive electrode which contains the hexagonal lithium-cobalt composite oxide for a lithium secondary cell as defined in Claim 1, as an active material.

[illegible]

—

Marked-Up Copy

Serial No:

Amendment Filed on:

3-26-2002

IN THE CLAIMS

--4. (Amended) The hexagonal lithium-cobalt composite oxide for a lithium secondary cell according to Claim 1, [2 or 3,] wherein the packing press density of the hexagonal lithium-cobalt composite oxide is from 2.90 to 3.35 g/cm³.

5. (Amended) A process for producing the hexagonal lithium-cobalt composite oxide for a lithium secondary cell as defined in [any one of Claims 1 to 4] Claim 1, which comprises dry blending a cobalt oxyhydroxide powder having an average particle size of from 1 to 20 μm and a specific surface area of from 2 to 200 m²/g, a lithium carbonate powder having an average particle size of from 1 to 50 μm and a specific surface area of from 0.1 to 10 m²/g, and a powder of an oxide of metal element M having an average particle size of at most 10 μm and a specific surface area of from 1 to 100 m²/g, and firing the mixture at a temperature of from 850 to 1,000°C in an oxygen-containing atmosphere.

7. (Amended) A positive electrode for a lithium secondary cell, which contains the hexagonal lithium-cobalt composite oxide for a lithium secondary cell as defined in [any one of Claims 1 to 4] Claim 1, as an active material.

9. (Amended) The positive electrode for a lithium secondary cell according to Claim 7 [or 8], wherein the current collector is aluminum or stainless steel.

10. (Amended) A lithium secondary cell employing a positive electrode which contains the hexagonal lithium-cobalt composite oxide for a lithium secondary cell as defined in [any one of Claims 1 to 4] Claim 1, as an active material.--

DESCRIPTION

LITHIUM-COBALT COMPOSITE OXIDE, PROCESS FOR ITS
PRODUCTION, POSITIVE ELECTRODE FOR LITHIUM SECONDARY CELL
EMPLOYING IT, AND LITHIUM SECONDARY CELL

5 TECHNICAL FIELD

The present invention relates to a lithium-cobalt
composite oxide for a lithium secondary cell, a process
for its production, a positive electrode for a lithium
secondary cell employing it, and a lithium secondary
10 cell.

BACKGROUND ART

In recent years, along with the progress in portable
or codeless equipments, a demand is mounting for a non-
aqueous electrolyte secondary cell which is small in size
15 and light in weight and has a high energy density. As an
active material for a non-aqueous electrolyte secondary
cell, a composite oxide of lithium and a transition
metal, such as LiCoO_2 , LiNiO_2 , $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$, LiMn_2O_4 or
 LiMnO_2 , has been known. Especially, a lithium secondary
20 cell employing a lithium-cobalt composite oxide (LiCoO_2)
as a positive electrode active material and employing a
lithium alloy or a carbon such as graphite or carbon
fiber as a negative electrode, provides a high voltage at
a level of 4 V and is widely used as a cell having a high
25 energy density.

However, a conventional lithium secondary cell has
had a problem of deterioration of the cycle

characteristics such that the cell discharge capacity gradually decreases as a charge/discharge cycle is repeated, or a problem that the safety is insufficient. Further, higher densification is required with respect to
5 the volume capacity density.

In order to improve such cell properties, JP-A-10-1316 proposes to use as an active material LiCoO_2 which is obtained by dispersing in an aqueous lithium hydroxide solution e.g. cobalt hydroxide or cobalt oxyhydroxide
10 wherein the valence of cobalt is trivalent, followed by heat treatment, for the purpose of improving the cycle characteristics, etc., of a lithium secondary cell.

Further, JP-A-10-279315 and JP-A-11-49519 propose to obtain a lithium secondary cell having a high capacity
15 and good cycle characteristics by using as an active material LiCoO_2 which is obtained by mixing e.g. dicobalt trioxide (Co_2O_3) or cobalt oxyhydroxide wherein the valence of cobalt is trivalent, with e.g. lithium oxide and firing such a mixture at a temperature of from 250 to
20 $1,000^\circ\text{C}$.

Further, JP-A-10-312805 proposes to improve the cycle characteristics of a lithium secondary cell by using as a positive electrode active material LiCoO_2 of a hexagonal system having a crystallite diameter of from 45
25 to 100 nm in a (110) direction of the crystallite, wherein the length of c axis of lattice constant is at most 14.051 \AA .

Further, JP-A-7-32017 proposes to use as a positive electrode active material LiCoO_2 having from 5 to 35% of Co atoms replaced with W, Mn, Ta, Ti or Nb, for improvement of the cycle characteristics of a lithium secondary cell. Further, JP-A-6-64928 proposes to improve the self-discharge characteristics of a lithium secondary cell by using as a positive electrode active material a Ti-containing lithium-cobalt composite oxide prepared by a synthesis employing a molten salt.

10 However, with respect to a lithium secondary cell using as a positive electrode active material a lithium-cobalt composite oxide, no product has been known which fully satisfies all of requirements for cycle characteristics, the initial weight capacity density, the stability and the low temperature operation efficiency, and for a production method for efficient mass production.

It is an object of the present invention to provide a lithium-cobalt composite oxide for a lithium secondary cell which has a large electric capacity and good discharge characteristics at low temperatures, is excellent in the charge/discharge cycle durability, and has an initial weight capacity density, a volume capacity density and high safety, a process for its production, a positive electrode for a lithium secondary cell employing it, and such a cell.

DISCLOSURE OF THE INVENTION

The present inventors have found that when a lithium-cobalt composite oxide having a specific composition and crystal structure, is used as a positive electrode for a lithium secondary cell, the cell properties will be excellent, and particularly, a lithium-cobalt composite oxide obtained by a specific production process is excellent in the productivity, and a lithium secondary cell wherein such a composite oxide is used as a positive electrode active material, is especially excellent in cycle characteristics and is also excellent in safety and low temperature operation efficiency.

The present invention provides a hexagonal lithium-cobalt composite oxide for a lithium secondary cell, which is represented by the formula $\text{LiCo}_{1-x}\text{M}_x\text{O}_2$, wherein x is $0 \leq x \leq 0.02$ and M is at least one member selected from the group consisting of Ta, Ti, Nb, Zr and Hf, and which has a half-width of the diffraction peak for (110) face at $2\theta = 66.5 \pm 1^\circ$, of from 0.070 to 0.180° , as measured by the X-ray diffraction using CuK_α as a ray source.

Further, the present invention provides a positive electrode for a lithium secondary cell, which contains the above hexagonal lithium-cobalt composite oxide for a lithium secondary cell, as an active material.

In the formula of the above lithium-cobalt composite oxide, if x is larger than 0.02 , the initial electric

capacity decreases, such being undesirable. Further, with a view to improvement of safety and production efficiency, x is preferably 0. Further, from the effects for improvement of cycle durability and low temperature operation efficiency, x is preferably $0.0005 \leq x \leq 0.02$, particularly preferably $0.001 \leq x \leq 0.01$, further preferably $0.002 \leq x \leq 0.007$.

The half-width of the diffraction peak for (110) face at $2\theta = 66.5 \pm 1^\circ$, as measured by the X-ray diffraction using CuK_α as a ray source, of the above lithium-cobalt composite oxide, reflects the crystallite diameter in a certain specific direction of the lithium-cobalt composite oxide, and a relation has been found such that the larger the half width of the peak, the smaller the crystallite diameter. In the present invention, the half-width of the peak means the width of the peak at $1/2$ of the height of the peak.

The half-width of the diffraction peak for (110) face of the lithium-cobalt composite oxide of the present invention is from 0.070 to 0.180° . If such a half-width is less than 0.070° , the charge/discharge cycle durability, initial electric capacity, average discharge voltage or safety of the cell employing it as a positive electrode active material, tends to deteriorate, such being undesirable. If such a half-width exceeds 0.180° , the initial electric capacity and safety of the cell tend to be low, such being undesirable. In a case where x is

at least 0.005, a particularly preferred range is from 0.100 to 0.165°. In a case where x is 0, from 0.070 to 0.110° is preferred, and a particularly preferred range is from 0.080 to 0.110°.

5 Further, the present invention provides a process for producing a hexagonal lithium-cobalt composite oxide for a lithium secondary cell, which comprises dry blending a cobalt oxyhydroxide powder having an average particle size of from 1 to 20 μm and a specific surface
10 area of from 2 to 200 m^2/g , a lithium carbonate powder having an average particle size of from 1 to 50 μm and a specific surface area of from 0.1 to 10 m^2/g , and a powder of an oxide of metal element M having an average
15 particle size of at most 10 μm and a specific surface area of from 1 to 200 m^2/g , which may be added as the case requires, followed by firing from 850 to 1,000°C in an oxygen-containing atmosphere, preferably from 4 to 30 hours.

In the present invention, the average particle size
20 means a weight average particle diameter. In the present invention, the average particle size is a particle size at a point where the cumulative curve of mass becomes 50% in the cumulative curve for the total mass of 100% prepared by obtaining the particle size distribution
25 based on mass. This may be referred to also as a mass base cumulative 50% diameter (for example, Chemical Engineering Handbook "Fifth Edition" (compiled by

Chemical Engineering Association) p 220-221, Kirk-Othmer, "Encyclopedia of Chemical Technology", 3rd. Edition, vol. 21, 106-113 (Wiley-Interscience). The measurement of the particle size is carried out by thoroughly dispersing in a medium such as water by means of e.g. ultrasonic treatment and measuring the particle size distribution (for example, by using Microtruck HRAX-100, manufactured by Nikkiso co., Ltd.).

For the process of the present invention, it is preferred to use the above-described specific cobalt oxyhydroxide as a cobalt material. If the average particle size of the cobalt oxyhydroxide is less than 1 μm , the safety of the cell tends to decrease, or the packing density of the electrode layer tends to decrease, whereby the electrical capacity per volume tends to decrease, such being undesirable. Further, if the average particle size of the cobalt oxyhydroxide exceeds 20 μm , the discharge characteristics of the cell at a large current tend to decrease, such being undesirable. A preferred average particle size of the cobalt oxyhydroxide is from 4 to 15 μm .

The above-described cobalt oxyhydroxide may sometimes be produced in a hydrous state. In such a case, the specific surface area can hardly be measured. Accordingly, in the present invention, the specific surface area of hydrous cobalt oxyhydroxide means the specific surface area with respect to a powder obtained

by drying the hydrate of cobalt oxyhydroxide at 120°C for 16 hours for dehydration. Further, when hydrous cobalt oxyhydroxide is to be used, it is preferred to use a powder after drying it. For example, it is preferred to employ it after drying at 120°C for 16 hours. In the present invention, if the specific surface area of the cobalt oxyhydroxide is less than 2 m²/g, the discharge capacity at a large current tends to decrease, such being undesirable. Further, if the specific surface area of the cobalt oxyhydroxide exceeds 200 m²/g, the packing density of the positive electrode layer tends to decrease, whereby the electric capacity per volume tends to decrease, such being undesirable. A preferred specific surface area of the cobalt oxyhydroxide is from 20 to 100 m²/g.

For the process of the present invention, it is preferred to use lithium carbonate having a specific nature, as a lithium material. If the average particle size of the lithium carbonate is less than 1 μm, the bulk density of the powder tends to decrease, and the productivity in mass production tends to decrease, such being undesirable. Further, if the average particle size of the lithium carbonate exceeds 100 μm, the initial electric capacity tends to decrease, such being undesirable. A particularly preferred average particle size of the lithium carbonate is from 5 to 30 μm. If the specific surface area of the lithium carbonate is less

than $0.1 \text{ m}^2/\text{g}$, the initial discharge capacity per unit weight tends to decrease, such being undesirable.

Further, if the specific surface area of the lithium carbonate exceeds $10 \text{ m}^2/\text{g}$, the packing density of the

5 positive electrode layer tends to decrease, whereby the electric capacity per volume tends to decrease, such being undesirable. A particularly preferred specific surface area of the lithium carbonate is from 0.3 to $3 \text{ m}^2/\text{g}$.

10 In the process for producing a lithium-cobalt composite oxide of the present invention, in a case where M is contained, it is preferred to use a metal oxide having a specific nature as a metal oxide containing element M, as a raw material. The metal oxide containing
15 element M may preferably be titanium oxide TiO_2 when M is titanium (Ti). Titanium oxide includes an anatase type, a rutile type, etc. It is particularly preferred to use an anatase type, since the cell properties will be good. When M is niobium (Nb), Nb_2O_3 may preferably be
20 mentioned. When M is tantalum (Ta), Ta_2O_5 may preferably be mentioned. When M is zirconium (Zr), zirconium oxide ZrO_2 may preferably be mentioned. When M is hafnium (Hf), HfO_2 may preferably be mentioned.

If the average particle size of the metal oxide
25 containing element M exceeds $10 \text{ }\mu\text{m}$, the distribution of element M in the lithium-cobalt composite oxide particles tends to be non-uniform, whereby the effects of adding

element M relating to the cell performance tend to decrease, such being undesirable. A preferred average particle size of the oxide of element M is at most 1 μm , particularly preferably at most 0.3 μm .

5 If the specific surface area of the metal oxide containing element M is less than 1 m^2/g , the reactivity tends to decrease, whereby the effects of adding element M relating to the cell performance tend to decrease, such being undesirable. On the other hand, if the specific
10 surface area of the metal oxide containing element M exceeds 100 m^2/g , element M tends to be uniformly incorporated into the crystal lattice, whereby the effects of adding element M relating to the cell performance tend to decrease, such being undesirable. A
15 preferred specific surface area of the oxide of element M is from 2 to 20 m^2/g .

 The lithium-cobalt composite oxide of the present invention is preferably obtained by preferably dry blending the cobalt oxyhydroxide powder, the lithium
20 carbonate powder and the oxide powder containing element M, followed by firing from 850 to 1,000°C preferably for from 4 to 30 hours in an oxygen-containing atmosphere. Wet blending is not preferred, since the productivity is low. If the firing temperature is lower than 850°C, the
25 charge/discharge cycle durability tends to be low, such being undesirable. On the other hand, if the firing temperature exceeds 1,000°C, the initial electric

capacity tends to decrease, such being undesirable.
 Particularly preferred is from 870 to 960°C, and more
 preferred is from 880 to 920°C. If the firing time is
 less than 4 hours, the firing state tends to be non-
 5 uniform during mass production, whereby fluctuation is
 likely to result in the properties, such being
 undesirable. If it exceeds 30 hours, the productivity
 tends to decrease, such being undesirable. It is
 particularly preferred to employ a firing time of from 8
 10 to 20 hours.

The firing of the above mixture is carried out
 preferably in an oxygen stream. The oxygen concentration
 in the stream is preferably from 10 to 100 volume%,
 particularly preferably from 19 to 50 volume%. If the
 15 oxygen concentration is low, the cell performance tends
 to deteriorate, such being undesirable.

A lithium secondary cell employing a positive
 electrode containing as an active material the lithium-
 cobalt composite oxide obtained by the process of the
 20 present invention and having the specific value of the
 half-width of the diffraction peak for (110) face, has a
 higher low temperature operation efficiency than ever,
 and is excellent in the charge/discharge cycle
 durability, while maintaining the initial electric
 25 capacity.

Among the lithium-cobalt composite oxides of the
 present invention, one wherein the packing press density

of the lithium-cobalt composite oxide is from 2.90 to 3.35 g/cm³, is preferred, since the capacity density per unit volume of the electrode layer of the positive electrode, can be made high. In the present invention, the packing press density means an apparent density of a press-molded product when the lithium-cobalt composite oxide powder is pressed under a load of 0.3 t/cm². If the packing press density is less than 2.90 g/cm³, the density of the electrode layer of the positive electrode tends to be low, whereby the capacity per volume tends to be low, such being undesirable. If the packing press density exceeds 3.35 g/cm³, the capacity development at a high current density of the cell tends to deteriorate, such being undesirable. The packing press density of the lithium-cobalt composite oxide is particularly preferably from 3.05 to 3.25 g/cm³.

In the lithium secondary cell of the present invention, it is preferred that a dispersion made of a kneaded product or a slurry comprising the powder of the lithium-cobalt composite oxide of the present invention, an electrically conductive material, a binder and a solvent or dispersant for the binder, is coated on a positive electrode current collector made of e.g. an aluminum foil or a stainless steel foil, and then dried to have it supported on the current collector to obtain a positive electrode. As the electrically conductive material, a carbon type conductive material such as

acetylene black, graphite or ketjenblack, is, for example, preferably employed. As the binder, polyvinylidene fluoride, polytetrafluoroethylene, polyamide, carboxymethyl cellulose or an acrylic resin
5 may, for example, preferably be employed. As the separator, a porous polyethylene film or a porous polypropylene film may, for example, preferably be employed.

In the lithium secondary cell of the present
10 invention, as the solvent for the electrolyte solution, a carbonic ester is preferred. The carbonic ester may be cyclic or chain. The cyclic carbonic ester may, for example, be propylene carbonate or ethylene carbonate (EC). The chain carbonic ester may, for example, be
15 dimethyl carbonate, diethyl carbonate (DEC), ethylmethyl carbonate, methylpropyl carbonate or methylisopropyl carbonate.

In the lithium secondary cell of the present invention, the above carbonic esters may be used alone or
20 in combination as a mixture of two or more of them. Further, such an ester may be mixed with other solvent. Further, depending upon the material for the negative electrode active material, there may be a case where the charge/discharge characteristics, cycle durability or
25 charge/discharge efficiency can be improved by a combined use of a chain carbonic ester and a cyclic carbonic ester.

Further, to such an organic solvent, a vinylidene fluoride/hexafluoropropylene copolymer (for example, Keiner, tradename, manufactured by Atochem Company) and vinylidene fluoride/perfluoropropyl vinyl ether copolymer disclosed in JP-A-10-294131, may be added, and the following solute may be added to obtain a gel polymer electrolyte.

As the solute for the above electrolyte solution or polymer electrolyte, it is preferred to use at least one member of lithium salts containing e.g. ClO_4^- , CF_3SO_3^- , BF_4^- , PF_6^- , AsF_6^- , SbF_6^- , CF_3CO_2^- or $(\text{CF}_3\text{SO}_2)_2\text{N}^-$ as an anion. For the above electrolyte solution or polymer electrolyte, it is preferred to add the electrolyte made of a lithium salt to the above solvent or solvent-containing polymer at a concentration of from 0.2 to 2.0 mol/l. If the concentration departs from this range, the ion conductivity tends to decrease, and the electrical conductivity of the electrolyte tends to decrease. The concentration is more preferably adjusted to be from 0.5 to 1.5 mol/l.

In the lithium secondary cell employing a positive electrode active material of the present invention, as the negative electrode active material, a material capable of absorbing and desorbing lithium ions, is employed. The material for such a negative electrode active material is not particularly limited, but, it may, for example, be a lithium metal, a lithium alloy, a

carbon material, an oxide composed mainly of a metal of Group 14 or 15 of the Periodic Table, a carbon compound, a silicon carbide compound, a silicon oxide compound, titanium sulfide or a boron carbide compound. As the
5 carbon material, one obtained by thermally decomposing an organic material by various thermal decomposition conditions, or artificial graphite, natural graphite, soil graphite, expanded graphite or scaly graphite, may, for example, be used. Further, as the oxide, a compound
10 composed mainly of tin oxide, may be used. As the negative electrode current collector, a copper foil or a nickel foil may, for example, be used.

The negative electrode in the present invention is obtained preferably by kneading the above-mentioned
15 negative electrode active material with an organic solvent in the same manner as in the case of the above positive electrode, to obtain a slurry, and coating the slurry on a metal foil current collector, followed by drying and pressing. There is no particular restriction
20 as to the shape of the lithium secondary cell of the present invention. A sheet shape (so-called film shape), folded-shape, wounded bottomed cylindrical shape or a button shape, may suitably be selected depending upon the particular application.

25 Now, the present invention will be described in further detail with reference to Examples, but it should be understood that the present invention is by no means

restricted to such Examples. The following Examples 1 to 14 are Examples of the present invention, and Examples 15 and 16 are Comparative Examples.

EXAMPLE 1

5 A cobalt oxyhydroxide powder having an average particle size of 10 μm and a specific surface area of 66 m^2/g , a lithium carbonate powder having an average particle size of 15 μm and a specific surface area of 1.2 m^2/g and an anatase-type titanium dioxide powder having
10 an average particle size of 0.22 μm and a specific surface area of 9 m^2/g , were mixed. The mixing ratio was such that the composition would be $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ after firing. These three types of powders were dry-blended and then fired at 910°C for 12 hours in an atmosphere
15 having the oxygen concentration adjusted to 28 volume% by adding oxygen gas to air.

With respect to the powder after the firing (the positive electrode active material powder), the X-ray diffraction spectrum was obtained by using RINT 2100
20 model X-ray diffraction apparatus, manufactured by Rigaku Corporation. By this powder X-ray diffraction using $\text{CuK}\alpha$ ray, a diffraction peak of a hexagonal system was obtained. Further, the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1^\circ$, was
25 0.121° .

This positive electrode active material powder was pressed under 0.3 t/cm^2 , and the packing press density

was determined from the volume and the weight and found to be 3.20 g/cm^3 . The $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ powder thus obtained, acetylene black and a polytetrafluoroethylene powder, were mixed in a weight ratio of 80/16/4 and
5 kneaded while adding toluene, followed by drying to obtain a positive electrode plate having a thickness of $150 \text{ }\mu\text{m}$.

And, two stainless steel simple closed cells were assembled in an argon glove box, by using an aluminum
10 foil having a thickness of $20 \text{ }\mu\text{m}$ as a positive electrode current collector, using a porous polypropylene film having a thickness of $25 \text{ }\mu\text{m}$ as a separator, using a metal lithium foil having a thickness of $500 \text{ }\mu\text{m}$ as a negative electrode, using a nickel foil of $20 \text{ }\mu\text{m}$ as a negative
15 electrode current collector, and using $1\text{M LiPF}_6/\text{EC}+\text{DEC}$ (1:1) as an electrolyte.

With respect to these two cells, firstly, charging was carried out to 4.3 V at a load current of 75 mA per g of the electrode active material at 25°C , and discharging
20 was carried out to 2.5 V at an applied current of 75 mA per g of the positive electrode active material, whereby the initial discharge capacity was obtained. With respect to one cell, the charge/discharge cycle test was further carried out 40 times. Further, the other cell
25 was charged at 25°C and then cooled to -10°C . Then, discharging was carried out to 2.5 V by a load current of 75 mA per g of the positive electrode active material,

whereby the initial discharge capacity at -10°C was obtained, and the capacity development rate at -10°C was obtained, on the basis that the initial electric capacity at 25°C was 100%.

- 5 The initial discharge capacity at from 2.5 to 4.3 V at 25°C was 149 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 95.3%. Further, the capacity developing rate at -10°C was 70%.

EXAMPLE 2

- 10 A cobalt oxyhydroxide powder having an average particle size of 10 μm and a specific surface area of 66 m^2/g , a lithium carbonate powder having an average particle size of 15 μm and a specific surface area of 1.2 m^2/g and an niobium oxide Nb_2O_5 powder having an average
15 particle size of 0.15 μm and a specific surface area of 5.3 m^2/g , were mixed. The mixing ratio was such that the composition would be $\text{LiCo}_{0.998}\text{Nb}_{0.002}\text{O}_2$ after firing. These three types of powders were dry-blended and then fired at
20 910°C for 12 hours in an atmosphere having the oxygen concentration adjusted to 28 volume% by adding oxygen gas to air.

- With respect to the powder after the firing (the positive electrode active material powder), the measurement was carried out in the same manner as in
25 Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1^{\circ}$, was 0.115° .

The packing press density of this positive electrode active material powder was determined in the same manner as in Example 1, and found to be 3.23 g/cm³.

Two stainless steel simple closed cells were assembled in the same manner as in Example 1 except that the above $\text{LiCo}_{0.998}\text{Nb}_{0.002}\text{O}_2$ powder was used instead of the $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ powder in Example 1.

With respect to these two cells, the measurement was carried out in the same manner as in Example 1, whereby the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 148 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 95.0%. Further, the capacity developing rate at -10°C was 73%.

EXAMPLE 3

A cobalt oxyhydroxide powder having an average particle size of 10 μm and a specific surface area of 66 m²/g, a lithium carbonate powder having an average particle size of 15 μm and a specific surface area of 1.2 m²/g and a tantalum oxide Ta_2O_5 powder having an average particle size of 0.23 μm and a specific surface area of 9.8 m²/g, were mixed. The mixing ratio was such that the composition would be $\text{LiCo}_{0.998}\text{Ta}_{0.002}\text{O}_2$ after firing. These three types of powders were dry-blended and then fired at 910°C for 12 hours in an atmosphere having the oxygen concentration adjusted to 28 volume% by adding oxygen gas to air.

With respect to the powder after the firing (the

positive electrode active material powder), the measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1^\circ$, was
5 0.115°.

The packing press density of this positive electrode active material powder was determined in the same manner as in Example 1, and found to be 3.19 g/cm³.

Two stainless steel simple closed cells were
10 assembled in the same manner as in Example 1 except that the above $\text{LiCo}_{0.998}\text{Ta}_{0.002}\text{O}_2$ powder was used instead of the $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ powder in Example 1.

With respect to these two cells, the measurement was carried out in the same manner as in Example 1, whereby
15 the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 148 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 96.1%. Further, the capacity developing rate at -10°C was 75%.

EXAMPLE 4

20 A cobalt oxyhydroxide powder having an average particle size of 8 μm and a specific surface area of 40 m²/g, a lithium carbonate powder having an average particle size of 22 μm and a specific surface area of 0.64 m²/g and an anatase-type titanium dioxide powder
25 having an average particle size of 0.17 μm and a specific surface area of 35 m²/g, were mixed. The mixing ratio was such that the composition would be $\text{LiCo}_{0.994}\text{Ti}_{0.006}\text{O}_2$

after firing. These three types of powders were dry-blended and then fired at 890°C for 15 hours in an atmosphere having the oxygen concentration adjusted to 19 volume% by adding oxygen gas to air.

5 With respect to the powder after the firing (the positive electrode active material powder), the measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1^\circ$, was
10 0.127°.

The packing press density of this positive electrode active material powder was determined in the same manner as in Example 1, and found to be 3.11 g/cm³.

Two stainless steel simple closed cells were
15 assembled in the same manner as in Example 1 except that the above $\text{LiCo}_{0.994}\text{Ti}_{0.006}\text{O}_2$ powder was used instead of the $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ powder in Example 1.

With respect to these two cells, the measurement was carried out in the same manner as in Example 1, whereby
20 the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 149 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 95.7%. Further, the capacity developing rate at -10°C was 72%.

EXAMPLE 5

25 A cobalt oxyhydroxide powder having an average particle size of 10 μm and a specific surface area of 66 m²/g, a lithium carbonate powder having an average

particle size of 15 μm and a specific surface area of 1.2 m^2/g and a zirconium oxide (ZrO_2) powder having an average particle size of 8.1 μm and a specific surface area of 15 m^2/g , were mixed. The mixing ratio was such that the composition would be $\text{LiCo}_{0.998}\text{Zr}_{0.002}\text{O}_2$ after firing. These three types of powders were dry-blended and then fired at 910°C for 12 hours in an atmosphere having the oxygen concentration adjusted to 28 volume% by adding oxygen gas to air.

10 With respect to the powder after the firing (the positive electrode active material powder), the measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1^\circ$, was
15 0.117°.

The packing press density of this positive electrode active material powder was determined in the same manner as in Example 1, and found to be 3.19 g/cm^3 .

Two stainless steel simple closed cells were
20 assembled in the same manner as in Example 1 except that the above $\text{LiCo}_{0.998}\text{Zr}_{0.002}\text{O}_2$ powder was used instead of the $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ powder in Example 1.

With respect to these two cells, the measurement was carried out in the same manner as in Example 1, whereby
25 the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 148 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 95.8%. Further, the

capacity developing rate at -10°C was 68%.

EXAMPLE 6

A cobalt oxyhydroxide powder having an average particle size of $10\text{ }\mu\text{m}$ and a specific surface area of $66\text{ m}^2/\text{g}$, a lithium carbonate powder having an average particle size of $15\text{ }\mu\text{m}$ and a specific surface area of $1.2\text{ m}^2/\text{g}$ and a hafnium oxide (HfO_2) powder having an average particle size of $0.4\text{ }\mu\text{m}$ and a specific surface area of $7.2\text{ m}^2/\text{g}$, were mixed. The mixing ratio was such that the composition would be $\text{LiCo}_{0.998}\text{Hf}_{0.002}\text{O}_2$ after firing. These three types of powders were dry-blended and then fired at 910°C for 12 hours in an atmosphere having the oxygen concentration adjusted to 28 volume% by adding oxygen gas to air.

With respect to the powder after the firing (the positive electrode active material powder), the measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1^{\circ}$, was 0.119° .

The packing press density of this positive electrode active material powder was determined in the same manner as in Example 1, and found to be 3.18 g/cm^3 .

Two stainless steel simple closed cells were assembled in the same manner as in Example 1 except that the above $\text{LiCo}_{0.998}\text{Hf}_{0.002}\text{O}_2$ powder was used instead of the $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ powder in Example 1.

With respect to these two cells, the measurement was carried out in the same manner as in Example 1, whereby the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 149 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 96.0%. Further, the capacity developing rate at -10°C was 70%.

EXAMPLE 7

A cobalt oxyhydroxide powder having an average particle size of 8 μm and a specific surface area of 40 m^2/g , a lithium carbonate powder having an average particle size of 22 μm and a specific surface area of 0.64 m^2/g and a zirconium oxide powder having an average particle size of 8.1 μm and a specific surface area of 16 m^2/g , were mixed. The mixing ratio was such that the composition would be $\text{LiCo}_{0.994}\text{Zr}_{0.006}\text{O}_2$ after firing. These three types of powders were dry-blended and then fired at 890°C for 15 hours in an atmosphere having the oxygen concentration adjusted to 19 volume% by adding oxygen gas to air.

With respect to the powder after the firing (the positive electrode active material powder), the measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1^\circ$, was 0.128°.

The packing press density of this positive electrode active material powder was determined in the same manner

as in Example 1, and found to be 3.10 g/cm^3 .

Two stainless steel simple closed cells were assembled in the same manner as in Example 1 except that the above $\text{LiCo}_{0.994}\text{Zr}_{0.006}\text{O}_2$ powder was used instead of the
5 $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ powder in Example 1.

With respect to these two cells, the measurement was carried out in the same manner as in Example 1, whereby the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 148 mAh/g, and the capacity retention after 40
10 charge/discharge cycles, was 95.7%. Further, the capacity developing rate at -10°C was 72%.

EXAMPLE 8

A cobalt oxyhydroxide powder having an average particle size of $10 \text{ }\mu\text{m}$ and a specific surface area of 66
15 m^2/g , and a lithium carbonate powder having an average particle size of $15 \text{ }\mu\text{m}$ and a specific surface area of $1.2 \text{ m}^2/\text{g}$, were mixed. The mixing ratio was such that the composition would be LiCoO_2 after firing. These three types of powders were dry-blended and then fired at 910°C
20 for 12 hours in an atmosphere having the oxygen concentration adjusted to 28 volume% by adding oxygen gas to air.

With respect to the powder after the firing (the positive electrode active material powder), the
25 measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1^\circ$, was

0.098°.

The packing press density of this positive electrode active material powder was determined in the same manner as in Example 1, and found to be 3.10 g/cm³.

5 Two stainless steel simple closed cells were assembled in the same manner as in Example 1 except that the above LiCoO₂ powder was used instead of the LiCo_{0.998}Ti_{0.002}O₂ powder in Example 1.

10 With respect to these two cells, the measurement was carried out in the same manner as in Example 1, whereby the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 149 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 94.8%. Further, the capacity developing rate at -10°C was 54%.

15 EXAMPLE 9

A cobalt oxyhydroxide powder having an average particle size of 15 μm and a specific surface area of 60 m²/g, and a lithium carbonate powder having an average particle size of 15 μm and a specific surface area of 1.2
20 m²/g, were mixed. The mixing ratio was such that the composition would be LiCoO₂ after firing. These two types of powders were dry-blended and then fired at 910°C for 12 hours in an atmosphere having the oxygen concentration adjusted to 28 volume% by adding oxygen gas
25 to air.

With respect to the powder after the firing (the positive electrode active material powder), the

measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1^\circ$, was 0.091° .

5 The packing press density of this positive electrode active material powder was determined in the same manner as in Example 1, and found to be 3.18 g/cm^3 .

Two stainless steel simple closed cells were assembled in the same manner as in Example 1 except that
10 the above LiCoO_2 powder was used instead of the $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ powder in Example 1.

With respect to one cell among them, charging was carried out to 4.3 V by a load current of 75 mA per g of the positive electrode active material at 25°C , and
15 discharging was carried out to 2.5 V at a load current of 75 mA per g of the positive electrode active material, whereby the initial discharge capacity was obtained. Further, with respect to this cell, the charge/discharge cycle test was continuously carried out 30 times. As a
20 result, the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 149 mAh/g, and the capacity retention after 30 charge/discharge cycles, was 96.3%.

Further, with respect to the other cell, charging was carried out to 4.3 V at a constant current of 0.2 mA
25 per 1 cm^2 of the positive electrode area and disassembled in the argon glove box, whereupon the positive electrode sheet after charging was taken out. The positive

electrode sheet was washed and then punched out in a size of 3 mm, and it was sealed together with EC in an aluminum capsule. The temperature was raised at a rate of 5°C/min by a scanning differential calorimeter, whereby the heat generation initiation temperature was measured. As a result, the heat generation initiation temperature was 165°C.

EXAMPLE 10

A cobalt oxyhydroxide powder having an average particle size of 8 μm and a specific surface area of 50 m^2/g , and a lithium carbonate powder having an average particle size of 15 μm and a specific surface area of 1.2 m^2/g , were mixed. The mixing ratio was such that the composition would be LiCoO_2 after firing. These two types of powders were dry-blended and then fired at 910°C for 12 hours in an atmosphere having the oxygen concentration adjusted to 28 volume% by adding oxygen gas to air.

With respect to the powder after the firing (the positive electrode active material powder), the measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1^\circ$, was 0.095° .

The packing press density of this positive electrode active material powder was determined in the same manner as in Example 1, and found to be 3.01 g/cm^3 .

Two stainless steel simple closed cells were assembled in the same manner as in Example 1 except that the above LiCoO_2 powder was used instead of the $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ powder in Example 1.

5 With respect to one of them, the initial electric capacity of the cell and the capacity after 30 cycles were obtained in the same manner as in Example 9, whereby the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 148 mAh/g, and the capacity retention after 30
10 charge/discharge cycles, was 97.0%.

Further, in the same manner as in Example 9, with respect to the other cell, the reactivity of the charged positive electrode active material with the electrolyte was determined, whereby the heat generation initiation
15 temperature was 169°C.

EXAMPLE 11

A cobalt oxyhydroxide powder having an average particle size of 12 μm and a specific surface area of 66 m^2/g , and a lithium carbonate powder having an average
20 particle size of 28 μm and a specific surface area of 0.43 m^2/g , were mixed. The mixing ratio was such that the composition would be LiCoO_2 after firing. These two types of powders were dry-blended and then fired at 890°C for 18 hours in an atmosphere having the oxygen
25 concentration adjusted to 19 volume% by adding oxygen gas to air.

With respect to the powder after the firing (the

positive electrode active material powder), the measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1^\circ$, was
5 0.083°.

The packing press density of this positive electrode active material powder was determined in the same manner as in Example 1, and found to be 3.12 g/cm^3 .

Two stainless steel simple closed cells were
10 assembled in the same manner as in Example 1 except that the above LiCoO_2 powder was used instead of the $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ powder in Example 1.

With respect to one of them, the initial electric capacity of the cell and the capacity after 30 cycles
15 were obtained in the same manner as in Example 9, whereby the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 148 mAh/g, and the capacity retention after 30 charge/discharge cycles, was 95.3%.

Further, in the same manner as in Example 9, with
20 respect to the other cell, the reactivity of the charged positive electrode active material with the electrolyte was determined, whereby the heat generation initiation temperature was 173°C .

EXAMPLE 12

25 LiCoO_2 was synthesized in the same manner as in Example 9 except that a cobalt oxide (Co_3O_4) powder having an average particle size of $8 \mu\text{m}$ and a specific

surface area of $0.66 \text{ m}^2/\text{g}$ was used instead of cobalt oxyhydroxide.

With respect to the powder after the firing (the positive electrode active material powder), the measurement was carried out in the same manner as in Example 9, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1^\circ$, was 0.133° .

The packing press density of this positive electrode active material powder was determined in the same manner as in Example 1, and found to be 2.75 g/cm^3 .

Two stainless steel simple closed cells were assembled in the same manner as in Example 1 except that the above LiCoO_2 powder was used instead of the LiCoO_2 powder in Example 9.

With respect to one of them, the initial electric capacity of the cell and the capacity after 30 cycles were obtained in the same manner as in Example 9, whereby the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 148 mAh/g , and the capacity retention after 30 charge/discharge cycles, was 96.4%.

Further, in the same manner as in Example 9, with respect to the other cell, the reactivity of the charged positive electrode active material with the electrolyte was determined, whereby the heat generation initiation temperature was 155°C .

EXAMPLE 13

LiCoO₂ was synthesized in the same manner as in the above Example 9 except that a cobalt oxyhydroxide powder having an average particle size of 30 μm and a specific surface area of 7 m^2/g was used instead of the cobalt oxyhydroxide powder having an average particle size of 15 μm and a specific surface area of 60 m^2/g .

With respect to the powder after the firing (the positive electrode active material powder), the measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1^\circ$, was 0.118° .

The packing press density of this positive electrode active material powder was determined in the same manner as in Example 1, and found to be 3.15 g/cm^3 .

Two stainless steel simple closed cells were assembled in the same manner as in Example 1 except that the above LiCoO₂ powder was used instead of the LiCoO₂ powder in Example 9.

With respect to one of them, the initial electric capacity of the cell and the capacity after 30 cycles were obtained in the same manner as in Example 9, whereby the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 137 mAh/g, and the capacity retention after 30 charge/discharge cycles, was 92.3%.

Further, in the same manner as in Example 9, with

respect to the other cell, the reactivity of the charged positive electrode active material with the electrolyte was determined, whereby the heat generation initiation temperature was 158°C.

5 EXAMPLE 14

LiCoO₂ was synthesized in the same manner as in the above Example 9 except that the firing at a temperature of 910°C for 12 hours in Example 9 was changed to the firing at 780°C for 12 hours.

10 With respect to the powder after the firing (the positive electrode active material powder), the measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1^\circ$, was
15 0.138°.

The packing press density of this positive electrode active material powder was determined in the same manner as in Example 1, and found to be 2.98 g/cm³.

Two stainless steel simple closed cells were
20 assembled in the same manner as in Example 1 except that the above LiCoO₂ powder was used instead of the LiCoO₂ powder in Example 9.

With respect to one of them, the initial electric capacity of the cell and the capacity after 30 cycles
25 were obtained in the same manner as in Example 9, whereby the initial discharge capacity at from 2.5 to 4.3 V at 25°C was 147 mAh/g, and the capacity retention after 30

charge/discharge cycles, was 96.5%.

Further, in the same manner as in Example 9, with respect to the other cell, the reactivity of the charged positive electrode active material with the electrolyte was determined, whereby the heat generation initiation temperature was 156°C.

EXAMPLE 15

$\text{LiCo}_{0.95}\text{Ti}_{0.05}\text{O}_2$ was synthesized in the same manner as in Example 1 except that the mixing ratio of the cobalt oxyhydroxide powder, the lithium carbonate powder and the anatase-type titanium dioxide powder was changed so that the composition would be $\text{LiCo}_{0.95}\text{Ti}_{0.05}\text{O}_2$ after firing.

With respect to the powder after the firing (the positive electrode active material powder), the measurement was carried out in the same manner as in Example 1, whereby the half-width of the diffraction peak for (110) face in the vicinity of $2\theta = 66.5 \pm 1^\circ$, was 0.188° .

Two stainless steel simple closed cells were assembled in the same manner as in Example 1 except that the above $\text{LiCo}_{0.95}\text{Ti}_{0.05}\text{O}_2$ powder was used instead of the $\text{LiCo}_{0.998}\text{Ti}_{0.002}\text{O}_2$ powder in Example 1.

With respect to these two cells, the measurement was carried out in the same manner as in Example 1, whereby the initial electric capacity at from 2.5 to 4.3 V at 25°C was 141 mAh/g, and the capacity retention after 40 charge/discharge cycles, was 93.6%. Further, the

CLAIMS

1. A hexagonal lithium-cobalt composite oxide for a lithium secondary cell, which is represented by the formula $\text{LiCo}_{1-x}\text{M}_x\text{O}_2$, wherein x is $0 \leq x \leq 0.02$ and M is at least one member selected from the group consisting of Ta, Ti, Nb, Zr and Hf, and which has a half-width of the diffraction peak for (110) face at $2\theta = 66.5 \pm 1^\circ$, of from 0.070 to 0.180° , as measured by the X-ray diffraction using CuK_α as a ray source.
2. The hexagonal lithium-cobalt composite oxide for a lithium secondary cell according to Claim 1, wherein x is $0.0005 \leq x \leq 0.02$, and the half-width of the diffraction peak for (110) face is from 0.100 to 0.165° .
3. The hexagonal lithium-cobalt composite oxide for a lithium secondary cell according to Claim 1, wherein x is 0 , and the half-width of the diffraction peak for (110) face is from 0.080 to 0.100° .
4. The hexagonal lithium-cobalt composite oxide for a lithium secondary cell according to Claim 1, 2 or 3, wherein the packing press density of the hexagonal lithium-cobalt composite oxide is from 2.90 to 3.35 g/cm^3 .
5. A process for producing the hexagonal lithium-cobalt composite oxide for a lithium secondary cell as defined in any one of Claims 1 to 4, which comprises dry blending a cobalt oxyhydroxide powder having an average particle size of from 1 to $20 \text{ }\mu\text{m}$ and a specific surface area of from 2 to $200 \text{ m}^2/\text{g}$, a lithium carbonate powder having an

average particle size of from 1 to 50 μm and a specific surface area of from 0.1 to 10 m^2/g , and a powder of an oxide of metal element M having an average particle size of at most 10 μm and a specific surface area of from 1 to 100 m^2/g , and firing the mixture at a temperature of from 850 to 1,000°C in an oxygen-containing atmosphere.

6. The process for producing the hexagonal lithium-cobalt composite oxide for a lithium secondary cell according to Claim 5, wherein the mixture is fired for from 4 to 30 hours.

7. A positive electrode for a lithium secondary cell, which contains the hexagonal lithium-cobalt composite oxide for a lithium secondary cell as defined in any one of Claims 1 to 4, as an active material.

8. The positive electrode for a lithium secondary cell according to Claim 7, having a mixture comprising the active material, an electrically conductive material and a binder, supported on a current collector.

9. The positive electrode for a lithium secondary cell according to Claim 7 or 8, wherein the current collector is aluminum or stainless steel.

10. A lithium secondary cell employing a positive electrode which contains the hexagonal lithium-cobalt composite oxide for a lithium secondary cell as defined in any one of Claims 1 to 4, as an active material.

11. The lithium secondary cell according to Claim 10, wherein a cyclic or chain carbonic ester is used as a

ABSTRACT

A composite oxide suitable for an active material of a positive electrode for a lithium secondary cell which can be used in a wide range of voltage, has a large
5 electric capacity and excellent low temperature performance and is excellent in the durability for charge-discharge cycles and highly safe, a process for its production, and a positive electrode and a cell employing it, are presented.

10 The composite oxide is a lithium-cobalt composite oxide which is represented by the formula $\text{LiCo}_{1-x}\text{M}_x\text{O}_2$, (wherein $0 \leq x \leq 0.02$ and M is at least one member selected from the group consisting of Ta, Ti, Nb, Zr and Hf), and which has a half-width of the diffraction
15 peak for (110) face at $2\theta = 66.5 \pm 1^\circ$, of from 0.070 to 0.180° , as measured by the X-ray diffraction using CuK_α as a ray source.

Declaration and Power of Attorney For Patent Application

特許出願宣言書及び委任状

Japanese Language Declaration

日本語宣言書

下記の氏名の発明者として、私は以下の通り宣言します。

私の住所、私書箱、国籍は下記の私の氏名の後に記載された通りです。

下記の名称の発明に関して請求範囲に記載され、特許出願している発明内容について、私が最初かつ唯一の発明者（下記の氏名が一つの場合）もしくは最初かつ共同発明者（下記の名称が複数の場合）であると信じています。

上記発明の明細書は、

- ☐ 本書に添付されています。
- ☐ ____月____日に提出され、米国出願番号または特許協定条約国際出願番号を____とし、
(該当する場合) ____に訂正されました。

私は、特許請求範囲を含む上記訂正後の明細書を検討し、内容を理解していることをここに表明します。

私は、連邦規則法典第37編第1条56項に定義されるとおり、特許資格の有無について重要な情報を開示する義務があることを認めます。

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled.

LITHIUM-COBALT COMPOSITE OXIDE,
PROCESS FOR ITS PRODUCTION, POSITIVE
ELECTRODE FOR LITHIUM SECONDARY CELL
EMPLOYING IT, AND LITHIUM SECONDARY
CELL

the specification of which

- ☐ is attached hereto.
- ☒ was filed on October 5, 2000
as United States Application Number or
PCT International Application Number
PCT/JP00/06959 and was amended on
____ (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56.

Japanese Language Declaration
(日本語宣言書)

私は、米国法典第35編119条 (a) - (d) 項又は365条 (b) 項に基づき下記の、米国以外の国の少なくとも一カ国を指定している特許協力条約365 (a) 項に基づく国際出願、又は外国での特許出願もしくは発明者証の出願についての外国優先権をここに主張するとともに、優先権を主張している、本出願の前に出願された特許または発明者証の外国出願を以下に、枠内をマークすることで、示しています。

Prior Foreign Application(s)

外国での先行出願

<u>11-287781</u>	<u>Japan</u>
(Number)	(Country)
(番号)	(国名)
<u>11-287785</u>	<u>Japan</u>
(Number)	(Country)
(番号)	(国名)
<u>2000-28860</u>	<u>Japan</u>

私は、第35編米国法典119条 (e) 項に基づいて下記の米国特許出願規定に記載された権利をここに主張いたします。

(Application No.)
(出願番号)

(Filing Date)
(出願日)

私は、下記の米国法典第35編120条に基づいて下記の米国特許出願に記載された権利、又は米国を指定している特許協力条約365条 (c) に基づく権利をここに主張します。また、本出願の各請求範囲の内容が米国法典第35編112条第1項又は特許協力条約で規定された方法で先行する米国特許出願に開示されていない限り、その先行米国出願書提出日以降で本出願書の日本国内または特許協力条約国際提出日までの期間中に入手された、連邦規則法典第37編1条56項で定義された特許資格の有無に関する重要な情報について開示義務があることを認識しています。

PCT/JP00/06959

October 5, 2000

(Application No.)
(出願番号)

(Filing Date)
(出願日)

(Application No.)
(出願番号)

(Filing Date)
(出願日)

私は、私自信の知識に基づいて本宣言書中で私が行なう表明が真実であり、かつ私の入手した情報と私の信じているところに基づく表明が全て真実であると信じていること、さらに故意になされた虚偽の表明及びそれと同等の行為は米国法典第18編第1001条に基づき、罰金または拘禁、もしくはその両方により処罰されること、そしてそのような故意による虚偽の声明を行なえば、出願した、又は既に許可された特許の有効性が失われることを認識し、よってここに上記のごとく宣誓を致します。

I hereby claim foreign priority under Title 35, United States Code, Section 119 (a)-(d) or 365(b) of any foreign application(s) for patent or inventor's certificate, or Section 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application for patent or inventor's certificate, or PCT International application having a filing date before that of the application on which priority is claimed.

Priority Claimed
優先権主張

<u>8/October/1999</u>	<input checked="" type="checkbox"/> Yes	<input type="checkbox"/> No
(Day/Month/Year Filed)	はい	いいえ
(出願年月日)		
<u>8/October/1999</u>	<input checked="" type="checkbox"/> Yes	<input type="checkbox"/> No
(Day/Month/Year Filed)	はい	いいえ
(出願年月日)		
<u>7/February/2000</u>	<u>YES</u>	

I hereby claim the benefit under Title 35, United States Code, Section 119(e) of any United States provisional application(s) listed below.

(Application No.)
(出願番号)

(Filing Date)
(出願日)

I hereby claim the benefit under Title 35, United States Code, Section 120 of any United States application(s), or Section 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of Title 35, United States Code Section 112, I acknowledge the duty to disclose information which is material to patentability as defined in Title 37, Code of Federal Regulations, Section 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of application.

Pending

(Status: Patented, Pending, Abandoned)
(現況: 特許許可済、係属中、放棄済)

(Status: Patented, Pending, Abandoned)
(現況: 特許許可済、係属中、放棄済)

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

$\frac{1}{\sqrt{2}} \begin{pmatrix} 1 & i \\ -1 & i \end{pmatrix}$

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith: *(list name and registration number)*

Office connected therewith: *(list name and registration number)*



Send Correspondence to:



Direct Telephone Calls to: (name and telephone number)

(703) 413-3000

100

Full name of sole or first joint inventor
Manabu Suhara

日付

Inventor's signature _____

Date _____

22 Feb 2022

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Full name of second joint inventor, if any
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第二の共同発明者の署名

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